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GB 2289061 A EP 0695815 A1 WO 91/20091 A1
US 5413642 A US 5314765 A US 4412901 A
WPI Accession no 81-24305D/14 & JP 0506014408 A

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FCVE FCVX FCXE FCXX FPCE FPCX FPDE FPDY FPFE
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(54) Deposition of lithium/lithium nitride on moving web

(57) In apparatus and a process for coating a web (W) by physical vapour deposition with at least one coating comprising lithium nitride a source of lithium is evaporated in a nitrogen atmosphere in a vacuum chamber. The web (W) is drawn in over a water cooled drum and lithium evaporated and deposited on the web. The reaction between lithium and nitrogen to form lithium nitride may be enhanced by utilising the technique of Ion Assisted Deposition. The web may be coated initially with copper or other electrically conductive materials. The apparatus and process may advantageously be used in the production of lithium dry cell batteries. In a modification at least one part is provided through which material may be introduced into the chamber manually.

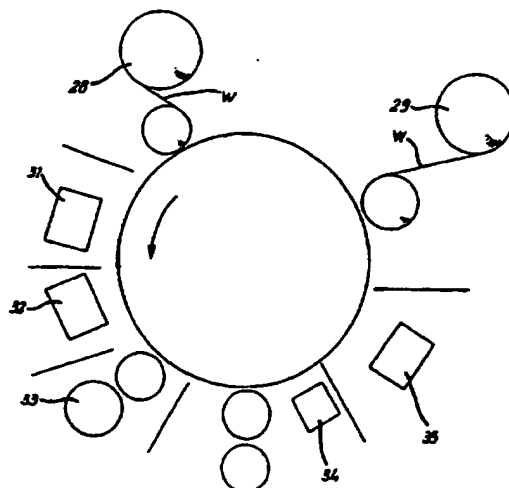
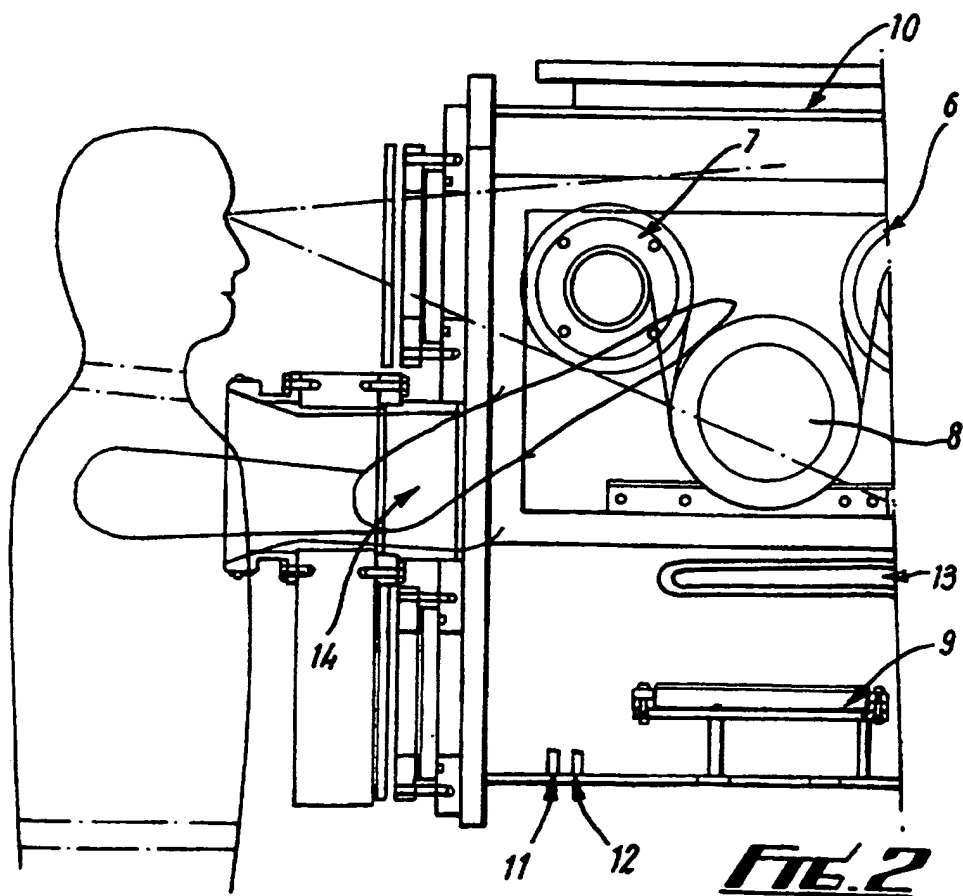
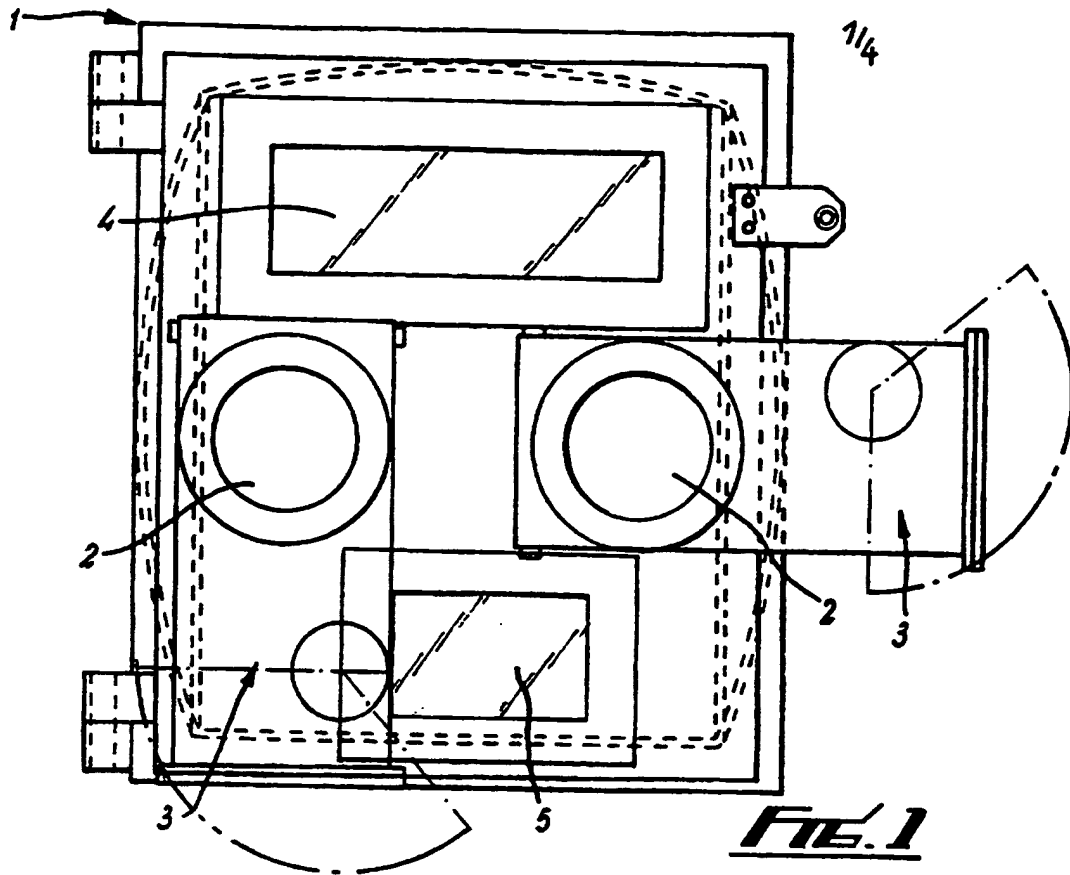


FIG. 3

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

The claims were filed later than the filing date within the period prescribed by Rule 25(1) of the Patents Rules 1995

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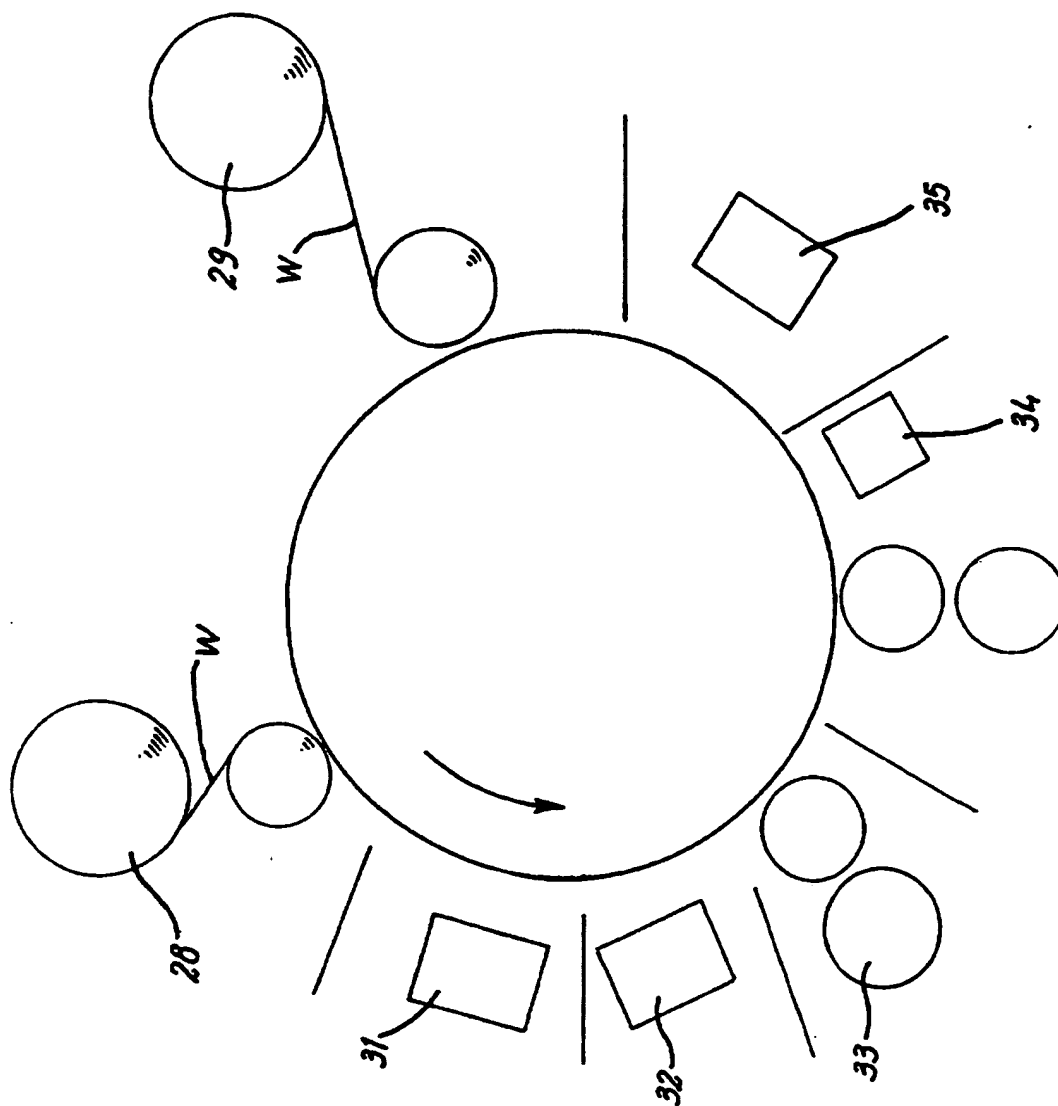


FIG. 3

FIG. 9

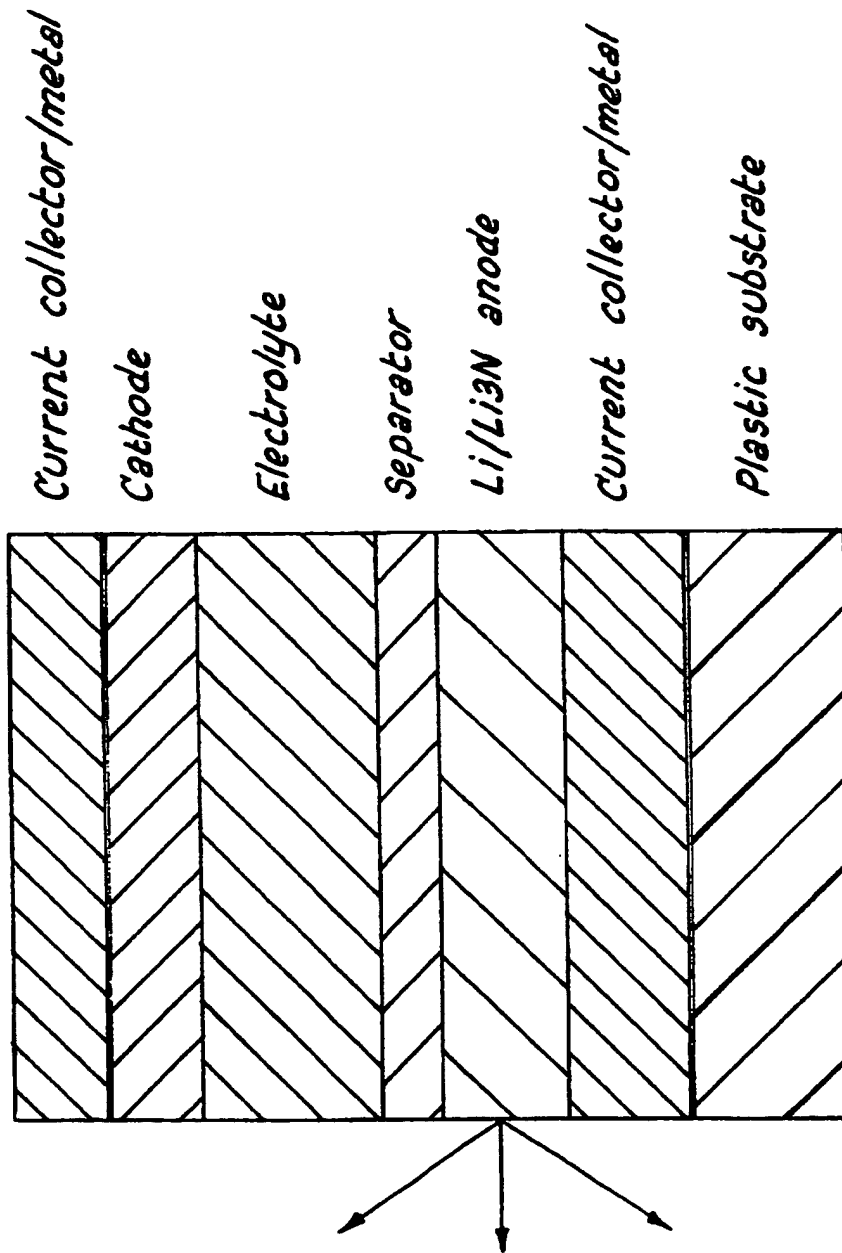


FIG. 9a

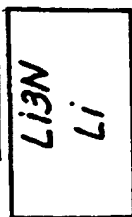


FIG. 9b

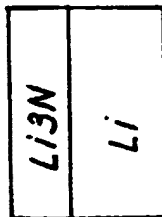
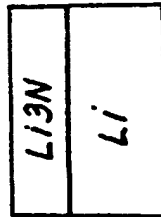
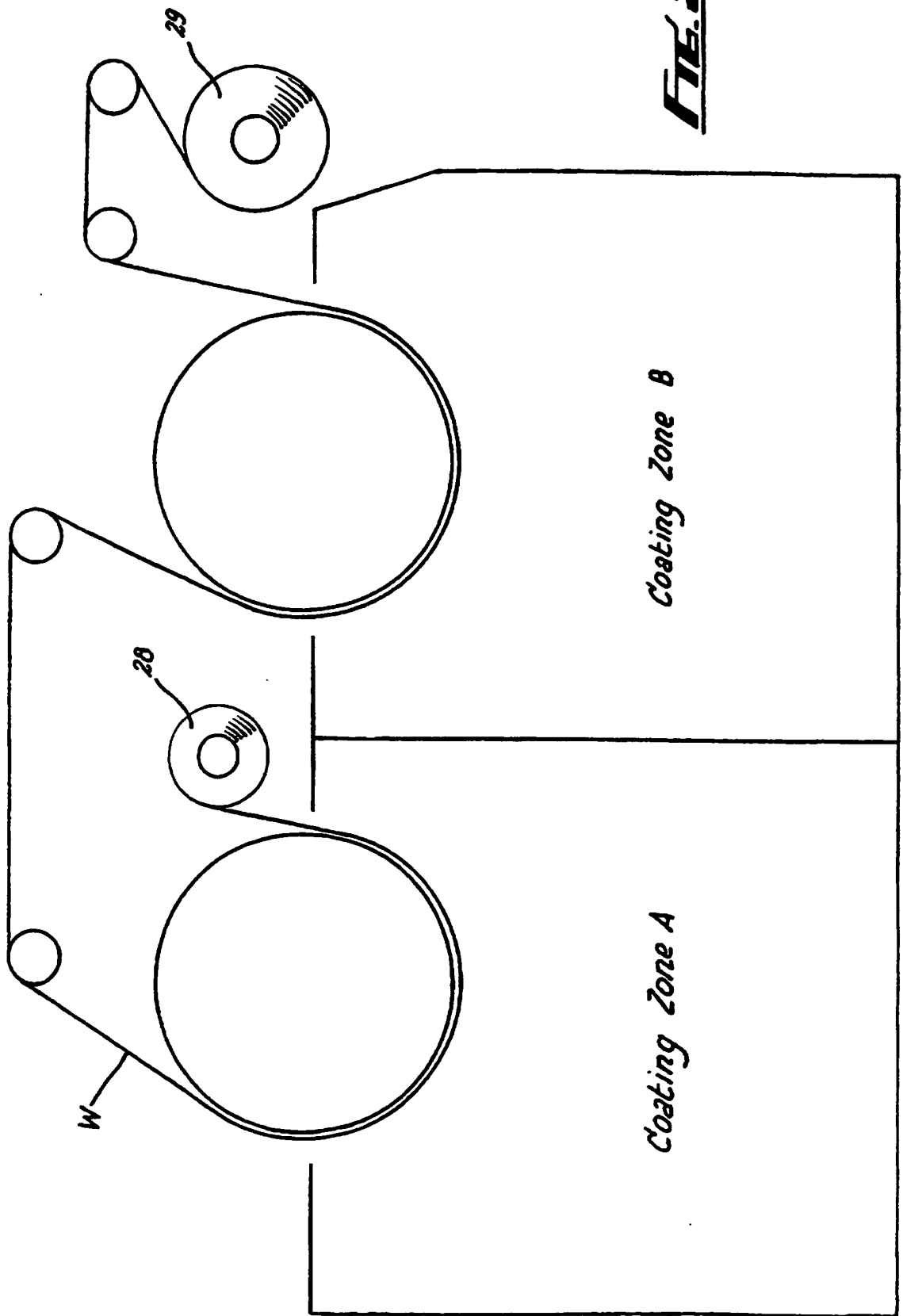


FIG. 9c



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FIG. 5



A VACUUM PROCESS AND APPARATUS FOR DEPOSITING
LITHIUM/LITHIUM NITRIDE COATING ON FLEXIBLE MOVING WEB

5 The present invention relates to a vacuum process and apparatus for depositing lithium/lithium nitride coating on flexible moving web.

BACKGROUND OF THE INVENTION

10 Lithium metal has been investigated and used as a metal anode in the fabrication of secondary "rechargeable" and primary non-rechargeable solid-state batteries. Most of these developments have been based on the utilisation of lithium anodes, solid cathodes and solid polymer electrolyte that both separates and provides the ionic pathway between the anode and cathode. However, the fundamental problem of this concept is the thermodynamic and kinetic instability of the lithium particularly during charging the cell. 15 This results in the dendritic growth of the lithium and the formation of poorly adherent high surface area deposit of lithium metal leading eventually to failure due to cell shorting. Various approaches to solve this problem have been investigated including the use of composite cathode consisting of vanadium oxide (V_2O_5) or titanium disulphide (TiS_2) plus carbon and a small amount of electrolyte. The problem 20

with such an approach is the swelling of the cathode upon the insertion of lithium in a host structure such as vanadium oxide.

Furthermore, when lithium discharges, oxidation of the anode gradually depletes the metal-electrolyte interface. It has also been

5 reported (see for example U.S. Patent Nos. 4,447,379 and 4,888,258) that the above problems can be eliminated by using

anodes made of lithium and nitrogen. The nitrogen is in the form of lithium nitride. The mixtures of The lithium/lithium nitride $\text{Li/Li}_3\text{N}$ are

intended to replace the lithium anodes in lithium based
10 electrochemical cells. This mixture has reduced

chemical/electrochemical activity towards electrolyte especially at the anode/electrolyte interface, can recycle lithium at very high

efficiencies and exhibits no cell voltage losses. The mixture significantly reduces the rate of interaction between elemental lithium

15 and the electrolyte during charge/discharge cycling and storage. In

U.S. Patent No. 4,888,258 by Desjardins et al the anode material was prepared by melting lithium metal foil in a crucible in an argon

filled dry box, adding nitrogen in the form of lithium nitride powder; nitrogen gas or other suitable nitrogen-containing material to form a

20 homogenous material, and cooling the material to room temperature.

The material was then compressed into the desired shape or rolled or

extruded into a thin foil. The anode material so formed comprised a solid solution of lithium metal and lithium nitride. It was claimed that a narrow range of about 0.1 to 10 mole percent N in the lithium was preferable for a satisfactory, homogenous anode material. The apparent limitation of this process however, is the difficulty of rolling or extruding this material into very thin lithium/lithium nitride foils at reasonably wide width and at economic prices required for the fabrication of rechargeable solid-state batteries.

According to one aspect of the present invention, there is provided apparatus for coating a web by physical vapour deposition in vacuum with a coating comprising lithium nitride, comprising a housing defining a vacuum chamber, a source of lithium in the chamber, a source of nitrogen in the chamber, and means for drawing a web past the source of lithium and the source of nitrogen whereby to coat the web with lithium nitride.

According to another aspect of the present invention, there is provided apparatus for coating a web comprising a housing defining a vacuum chamber, a coating station disposed in the vacuum chamber, means for transporting the web past the coating station in the vacuum chamber, at least one port through which material may be introduced into the chamber manually when the pressure in the

vacuum chamber is at or near atmospheric and valve means for closing off the or each port.

According to a further aspect of the present invention, there is provided a process of coating a web with a coating comprising lithium nitride in a vacuum chamber including the steps of introducing
5 nitrogen into the vacuum chamber, evaporating lithium or lithium nitride from a lithium or lithium nitride respectively source within the chamber and moving a web past the source to produce the said coating on the said web.

10 In a preferred embodiment of the apparatus of the invention, there are two glove ports. Each glove port has an associated valve, which is advantageously a gate valve, to isolate the corresponding port from the vacuum chamber. The valves may be manual, pneumatic or solenoid type. The means for transporting the web in
15 the vacuum chamber comprises an unwind drive, and a wind drive. These means are operative to transport the web at various speeds under controlled tension. A water cooled drum is provided to cool the web. Means are provided for evaporating lithium within the vacuum chamber. These means may comprise an evaporation boiler, thermal
20 resistance boats, electron beam guns, sputtering sources, induction sources, nozzle evaporators or lasers. Means are provided for

admitting gases into the vacuum chamber. These means may comprise gas feedthroughs connected to mass flow controllers. Electrodes are provided to enable the nitrogen/argon gas mixture to be ionized using, for example D.C. RF or microwave power. The electrodes comprise glow discharge cathodes disposed between the web and the evaporation source. Means are provided to enable the web to be coated initially with copper or other electrically conductive materials.

In a preferred embodiment of the method of the invention web is loaded into the chamber which is then pumped down to a low vacuum prior to admitting argon to atmospheric pressure. Lithium metal is then loaded into an evaporation source. Precise amounts of gases are introduced into the chamber at predetermined flows.

Lithium/lithium nitride layer is deposited on a polymer or other substrate web using the Physical Vapour Deposition (PVD) as a vacuum coating process. In this process the thickness and the composition of the deposited lithium/lithium nitride layer can be varied according to requirements. The reaction between lithium and nitrogen may be enhanced by utilising the technique of Ion Assisted Deposition (IAD) in which nitrogen is present as a highly ionised reactant. Therefore, lithium/lithium nitride coating can be formed by

adding controlled amount of nitrogen to the deposited lithium or lithium nitride on a moving web inside a vacuum chamber. This can be arranged to form either a solid solution of lithium/lithium nitride or multi-layered coating of lithium and lithium nitride. The nitrogen is mixed with argon in the vacuum chamber and this mixture is ionised by DC, RF or microwave power applied to electrodes. The tension and speed of the web is adjusted as desired. The web is coated initially with copper or other electrically conductive materials. Lithium can be reacted with nitrogen atom or ions at various nitrogen concentrations to form lithium nitride coating on the moving web. Lithium nitride can be formed within the lithium matrix at fixed or graded concentrations using molecular nitrogen, plasma reaction and/or pulsed gas process. Multi-layered coating of lithium/lithium nitride can also be formed.

Any number of separate coating zones may be provided to sequentially deposit layers of copper or other electrically conductive materials, lithium/lithium nitride anode, separator, electrolyte, EB curing and top cathode.

The process may comprise a roll system such as a 3-5 hydrophilic gravure roll system for applying thin films of monomers or other materials and curing them with an electron beam gun in

vacuum such as a 10-50 keV gun in vacuum. Separator and electrolytes can also be deposited using atomizers, flash evaporation or plasma deposition.

5 Stripe metallising may be applied to produce narrow, clear lanes on the moving web to enable electrical connection to be made to the finished battery cell in vacuum.

In order that the invention may be more clearly understood, embodiments thereof will now be described, by way of example with reference to the accompanying drawings in which:-

10 Figure 1 is a front elevational view of apparatus for coating according to the invention,

Figure 2 is a partial side elevational view in section according to the invention,

15 Figure 3 shows diagrammatically one form of web coater for dry cell production,

Figure 4 shows diagrammatically one form of dry cell fabrication which can be made in the web coater of figure 3,

20 Figure 4a shows schematically one form of lithium/lithium nitride anode comprising lithium nitride deposited within a matrix of lithium,

Figure 4b shows schematically another form of lithium/lithium

nitride anode comprising a deposit of lithium and a deposit of lithium nitride,

Figure 4c shows schematically a further form of lithium/lithium nitride anode comprising a graded concentration of lithium within a lithium matrix, and

Figure 5 shows schematically a double sided vacuum coater for dry cell production.

Detailed description of the invention

Lithium/lithium nitride coating is deposited on a moving polymer or other web inside a vacuum chamber. Copper foil or a polymer web initially coated with sufficient thickness of aluminium, copper or other metals can be used. For this purpose a vacuum coating apparatus is provided with a dry glove box as illustrated in figures 1 and 2. The front door 1 has two glove ports 2 isolated from the vacuum chamber by two gate valves 3. The door also has two windows 4 and 5. The top window 4 is used to view the process while the bottom window 5 houses a light source to provide lighting inside the vacuum chamber during loading/unloading of the web. Manual, pneumatic or solenoid type gate valves can be used in glove ports 2 to the chamber. The vacuum chamber also has an unwind drive 6, rewind drive 7 and water cooled drum 8 to move the polymer

or other web at various speeds under controlled tension. The evaporation source 9 consists of a specially designed high evaporation boiler (U.S. Patent Nos. NEC 37833/MX and NEC 37834/MX) to evaporate lithium or lithium nitride. Other sources that can also be used include thermal resistance boats, electron beam guns, sputtering sources, induction sources, nozzle evaporators or lasers. The chamber 10 also contains two gas feedthroughs 11, 12 connected to mass flow controllers to admit precise amounts of gases at predetermined flows into the vacuum chamber. High voltage electrodes 13 such as rods or plates are used to ionise the nitrogen/argon gas mixture. DC, RF or microwave power can be applied on the electrodes. The process starts by loading polymer or other web on the unwind drive 6 inside the vacuum chamber which is then pumped down to a low vacuum prior to admitting argon to atmospheric pressure. Lithium metal or lithium nitride is then loaded into the evaporation source by opening the gate valves and pushing gloves 14 in glove ports 2 into the chamber which is filled with argon gas. This method is used to minimize lithium reaction if loading is carried out in air. Lithium or lithium nitride is loaded by opening the lithium or lithium nitride canister inside the argon filled chamber. The gate valves 3 are then closed and the chamber is pumped down again

to high vacuum to obtain air free atmosphere. Coating cycle starts by adjusting the tension of the polymer or other web which is moving at a preset speed. Lithium or lithium nitride is then evaporated by heating up the crucibles or the high rate evaporation boiler to the required preset temperature. During evaporation lithium is passing through and reacting with the nitrogen/argon plasma to deposit lithium/lithium nitride on the web. Lithium/lithium nitride may be formed in various ways. Lithium nitride may be deposited within a matrix of lithium as shown in figure 4a. Multi-layered lithium/lithium nitride coating may be deposited as shown in figure 4b by passing the moving web into two coating zones. The first zone can be used to deposit lithium while the second is used to deposit lithium nitride. A graded concentration of lithium nitride may be deposited within a lithium matrix by using a gas pulsing technique as shown in figure 4c. In this technique reactive gas such as nitrogen is pulsed at a controlled pulse rate into argon gas plasma. As the nitrogen pulse decays, the concentration of nitrogen starts to decrease to a minimum. Therefore, upon the initiation of the pulse a high concentration of lithium nitride can be deposited following which the concentration in the lithium matrix decreases as the pulse decays. To minimize the heat load on the web that results from the deposited

film and the radiant heat from the source the drum can be cooled to typically -25°C. This is also useful for the incorporation of multiple deposition sources to enable thicker deposits to be laid down at higher line speeds. Furthermore, the use of two deposition sources in respective coating zones A and B would enable both sides of the web W to be coated in the same machine pass as shown in Figure 5. Coating zones A and B each comprises elements corresponding to items 31 to 35 of figure 3. After depositing the required coating the chamber is vented with moisture free, zero grade argon gas (99.996% purity) to atmospheric pressure. The gate valves 3 are then opened and the gloves 14 pushed into the chamber. The coated web is removed from the rewind drive 7 and dropped into the canister which is then sealed with the top lid inside the argon filled chamber without exposing the coated web to air.

The principles which are applied to the development machine can be scaled up and used on larger industrial web coating machines. The whole process of fabricating lithium dry cell batteries can be carried out inside the vacuum chamber without exposing the coated web to air. Figure 4 shows a schematic diagram of the proposed dry cell fabrication than can be carried out inside the web coater. Figure 3 shows a schematic diagram of a vacuum web coater that can be

used for the industrial production of lithium dry cells. The web coater comprising an unwind drive 28 and rewind drive 29 and six or more coating zone 31 to 35 for the deposition of various materials. The moving web W is coated initially with copper or other electrically
5 conductive material in the first zones 31. Then it moves to the second zone 32 where anodes such as lithium/lithium nitride coating can be evaporated in a reactive environment as described above. Anodes may also comprise composite materials of which Li/Li₃N is one component as indicated in U.S. Patent No. 4,888,258. For example,
10 anode compositions comprising plastic or elastomeric macromolecular material with electronic conduction, lithium alloys and carbon compounds are described in U.S. Patent No. 4,517,265 to Belanger et al. Similar anode compositions may be made according to U.S. Patent 4,888,258 which would include Li/Li₃N as a component.
15 Similarly, anode material may be made according to U.S. Patent No. 4,002,492 to Rao using mixtures of Li/Li₃N and lithium; aluminium alloys or mixtures of lithium nitride and lithium-aluminium alloys. The same process can be used to deposit mixtures of lithium nitride and one or more lithium alloys such as Li-Si, Li-Sn, Li-Fe, Li-Sb, Li-Bi, Li-Pb, Li-As and other combinations as thereof as anode materials. The
20 third zone 33 is used to deposit a separator layer using porous

polypropylene and glass microfibre materials that are sufficiently porous and wettable by the appropriate electrolyte. Other porous materials can also be used as a separator layer. Gravure roll coating, atomizers or flash evaporation can be used to deposit the separator layer. The fourth zone 34 uses gravure roll coating, atomizers or flash evaporation to deposit various types of electrolytes. These can include nonaqueous solvent systems such as dioxolanes, furans, glymes, methoxymethanes, glycol sulfites, sulfolanes, propylene carbonate and other combinations as indicated in the U.S. Patent No. 4,888,258. Other polymers can be deposited by gravure roll coating, atomizers or flash evaporation, then cured in the fifth zone 35 with electron beam (EB) gun of moderate power (10-50KeV). The final cathode material is deposited in the sixth zone 35 using sputtering, thermal resistive or electron beam evaporation. Materials such as those indicated in U.S. Patent No. 4,888,258 that includes a chalcogen or chalcogenide compound of transition metal can be used. Other intercalation-type materials and transition metal sulphides such as TiS_2 , MoS_2 or oxides such as V_6O_{13} are preferred. The technique of stripe metallising can also be applied to the production of thin dry cell batteries. In this process narrow, clear lanes are produced running in the machine direction which enable the electrical

connection to be made by end spraying the current collector of the finished cell battery.

It will be appreciated that the above embodiments have been described by way of example only and that many variations are possible without departing from the scope of the invention.

CLAIMS

1. Apparatus for coating a web by physical vapour deposition in vacuum with a coating comprising lithium nitride, comprising a housing defining a vacuum chamber, a source of lithium in the chamber, a source of nitrogen in the chamber, and means for drawing a web past the source of lithium and the source of nitrogen whereby to coat the web with lithium nitride.
2. Apparatus for coating a web comprising a housing defining a vacuum chamber, a coating station disposed in the vacuum chamber, means for transporting the web past the coating station in the vacuum chamber, at least one port through which material may be introduced into the chamber manually when the pressure in the vacuum chamber is at or near atmospheric and valve means for closing off the or each port.
3. Apparatus as claimed in claim 1 or 2, in which there are two glove ports extending into the vacuum chamber.
4. Apparatus as claimed in claim 3, in which a valve is associated with each glove port to enable the corresponding port to be isolated from the vacuum chamber.
5. Apparatus as claimed in claim 4, in which each associated valve is a gate valve.

6. Apparatus as claimed in claim 3 or 4 in which each valve is manually operable.

7. Apparatus as claimed in claim 3 or 4, in which each valve is pneumatically operable.

5 8. Apparatus as claimed in claim 3 or 4, in which each valve is solenoid operable.

9. Apparatus as claimed in any preceding claim in which the means for transporting the web in the vacuum chamber comprises an unwind drive and a wind drive.

10 10. Apparatus as claimed in claim 9, in which the means for transporting is operative to transport the web at various speeds under controlled tension.

11. Apparatus as claimed in any preceding claim, in which a water cooled drum is provided to cool the web.

15 12. Apparatus as claimed in any preceding claim, in which means are provided for evaporating lithium within the vacuum chamber.

13. Apparatus as claimed in claim 12, in which the means for evaporating lithium comprise an evaporation boiler.

20 14. Apparatus as claimed in claim 12, in which the means for evaporating comprise thermal resistance boats.

15. Apparatus as claimed in claim 12, in which the means for

vap rating comprise lectr n beam guns.

16. Apparatus as claimed in claim 12, in which the means for evaporating comprises sputtering sources.

17. Apparatus as claimed in claim 12, in which the means for evaporating comprises induction sources.

18. Apparatus as claimed in claim 12, in which the means for evaporating comprises nozzle evaporators.

19. Apparatus as claimed in claim 12, in which the means for evaporating comprise lasers.

20. Apparatus as claimed in any preceding claim in which means are provided for admitting gas into the vacuum chamber.

21. Apparatus as claimed in claim 20, in which the means for admitting gas comprise gas feedthroughs connected to mass flow controllers.

22. Apparatus as claimed in any preceding claim, in which electrodes are provided to enable a gas mixture, in the vacuum chamber to be ionized.

23. Apparatus as claimed in any preceding claim, in which means are provided to enable the web to be coated with an electrically conductive material.

24. Apparatus f r coating a web substantially as hereinbefore

described with reference to figures 1 and 2, or to figure 3 or to figure 5 of the accompanying drawings.

5 25. A process of coating a web with a coating comprising lithium nitride in a vacuum chamber including the steps of introducing nitrogen into the vacuum chamber, evaporating lithium or lithium nitride from a lithium or lithium nitride respectively source within the chamber and moving a web past the source to produce the said coating on the said web.

10 26. A process as claimed in claim 25 or 26, in which the reaction between lithium and nitrogen is enhanced by utilising the technique of ion assisted deposition in which nitrogen is present as an ionised reactant.

27. A process as claimed in claim 25, in which the nitrogen is mixed with argon and the resultant mixture ionised.

15 28. A process as claimed in claim 27, in which the resultant mixture is ionised by DC, RF or microwave power applied to electrodes.

29. A process as claimed in claim 25, 26, 27 or 28 in which the web is coated initially with an electrically conductive material.

20 30. A process as claimed in any of claims 25 to 29, in which multiple layers of lithium/lithium nitride are formed on the web.

31. A process of coating a web substantially as hereinbefore described with reference to the accompanying drawings.



Application No: GB 9621109.9 **Examiner:** Peter Beddoe
Claims searched: 1, in part 3-24, 25-30 & in part 31 **Date of search:** 14 January 1998

Patents Act 1977
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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

**UK CI (Ed.P): C7F (FCSE, FCSX, FCVE, FCVX, FCXE, FCXX, FCAS, FCAV,
FCAX, FPCE, FPCX, FPDE, FPDY, FPPE, FPPEX)**

Int Cl (Ed.6): C23C (14/00, 14/06, 14/24, 14/34, 14/56); H01M 6/18

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
Y	EP 0695815 A1 (LEYBOLD) see esp col3 lines 22-37 & fig	1,25
Y	WO 91/20091 A1 (GENERAL) see esp fig 1	1,25
Y	US 5413642 (ALGER) see esp col9 lines 8-40	1,25
Y	US 5314765 (MARIETTA) see esp col2 line 59 - col3 line 2	1,25
Y	US 4412901 (FREUDENBERG) see esp claim 1 & exs	1,25
A	GB 2289061 A (ION COAT) see whole doc	
Y	WPI Accession no 81-24305D/14 & JP 56014408 A (TOKYO) see abstract	1,25

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